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The Electric Moments of Organic Peroxides. II. Aliphatic Peracids¹BY JAMES R. RITTENHOUSE, WALTER LOBUNEZ, DANIEL SWERN² AND JOHN G. MILLER

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The electric dipole moments of five long-chain aliphatic peracids have been measured in benzene. Within experimental error, all five have the same moment, 2.32 D. The molecular weights of two of these acids in benzene have been determined cryoscopically and show that these acids are monomeric in solution. The results indicate considerable puckering in the five-membered chelate ring formed by hydrogen bonding between the hydroxyl oxygen and the carbonyl oxygen atoms.

Recently, Davison³ discovered strong infrared spectroscopic evidence that perbenzoic acid exists normally in monomeric form due to an intramolecular hydrogen bond between the carbonyl oxygen and the hydroxyl oxygen atoms of the percarboxyl group. Giguère and Olmos⁴ found the same chelation in aliphatic peracids by their measurements of the infrared spectra of performic and peracetic acids. They estimated that the attraction of the carbonyl oxygen atom for the hydroxyl hydrogen atom is sufficient to overcome most of the potential barrier restricting rotation about the O-O bond. Their data were not sufficient to decide whether the chelate ring formed by this hydrogen bonding is planar or puckered. In addition to the spectroscopic information they pointed to the greater volatility and more normal entropy of vaporization of the peracids as compared to the ordinary carboxylic acids in support of the chelation. They also suggested that the instability of these short chain aliphatic peracids may be due in part to the strain caused by the chelation.

Emanuel and co-workers⁵ also obtained chemical and infrared spectroscopic evidence that the lower aliphatic peracids are strongly chelated at room temperature or below, the chelation rendering these substances more readily combusted. Their explanation of the role of the hydrogen bonding in combustion recalls the mechanism proposed by Bartlett⁶ for the reaction of perbenzoic acid with olefins.

More recently, Swern, Witnauer, Eddy and Parker⁷ studied the infrared adsorption of long-chain aliphatic peracids in solution and in the solid state and also the X-ray diffraction patterns of these acids in the solid state. Their data showed that in solution the peracids exist nearly exclusively as monomers, being strongly chelated by the hydrogen bonding proposed earlier. In the solid state, these

chelated structures form dimers by weak intermolecular hydrogen bonding. They found strong additional evidence for the monomers in solution by cryoscopic measurement of the molecular weight of perlauric acid in benzene. Furthermore, they found that the chelation weakens the acid strength of the peracids. They were not able to tell whether the chelate rings are puckered or planar.

The study of the dipole moments of peracids reported here was undertaken to obtain additional information on the chelation and the extent of puckering, if any, in the five-membered ring. The molecular weights of two of the acids also were measured.

Experimental and Results

The peracids were prepared and purified at the Eastern Regional Laboratory as described earlier.⁸ The dipole moments were measured as described in the first article⁹ in this series and the symbols used in Table I, which gives the results, are as explained in that article. A Beckmann apparatus was used to measure the freezing point depressions in benzene solutions. The stirring in it was mechanical and supercooling was controlled readily. Over the weight fraction range 0.001 to 0.005, which falls within the range of concentrations used for the moment measurements, perpelargonic showed a molecular weight of 173.7, compared with the monomeric formula weight 174.2 and perpalmic acid had a molecular weight of 273.1, the monomeric formula weight being 272.4. In addition, for the polarization measurements, the Hoecker plots of P_2w_2 against w_2 were good straight lines passing through the origin, showing that the acids are largely unassociated.

An unsuccessful effort was made to obtain the moment of perbenzoic acid. The dielectric constant values increased with time showing that some decomposition was taking place during the measurements. In contrast, the aliphatic peracids were quite stable. After the dielectric constant run for perlauric acid at 50°, the same solutions were run two days later at 30° and the values obtained at that time agreed nearly exactly with those determined at 30° in an earlier run.

Discussion

The dipole moments reported here are the first recorded for aliphatic peracids. The mean of the seven determinations for the five acids studied is 2.32 D with a mean deviation of ± 0.04 D, showing that these peracids all have the same moment within experimental error. The new molecular weight determinations add to the earlier evidence that these acids are strongly chelated by hydrogen bonding. The dipole moment data may now be used to investigate the puckering of the five-membered chelate ring.

(8) W. E. Parker, C. Ricciuti, C. L. Ogg and D. Swern, *ibid.*, **77**, 4037 (1955).

(9) W. Lobunez, J. R. Rittenhouse and J. G. Miller, *ibid.*, **80**, 3505 (1958).

(1) A report of work done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act of 1946. The contract is being supervised by the Eastern Utilization Research and Development Division of the Agricultural Research Service.

(2) Eastern Regional Research Laboratory.

(3) W. H. T. Davison, *J. Chem. Soc.*, 2456 (1951).

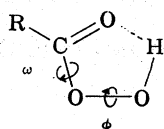
(4) P. A. Giguère and A. W. Olmos, *Can. J. Chem.*, **30**, 821 (1952).

(5) Z. K. Maizus, G. Ya. Timofeeva and N. M. Emanuel, *Doklady Akad. Nauk S. S. S. R.*, **70**, 655 (1950); Z. K. Maizus, V. M. Cherednichenko and N. M. Emanuel, *ibid.*, **70**, 855 (1950); B. S. Neporent, T. B. Pavlovskaya, N. M. Emanuel and N. G. Yaroslavskii, *ibid.*, **70**, 1025 (1950); D. G. Knorre and N. M. Emanuel, *Zhur. Fiz. Khim.*, **26**, 425 (1952).

(6) P. D. Bartlett, *Rec. Chem. Progr.* (Kresge-Hooker Sci. Library), **11**, No. 1, 47 (1950).

(7) D. Swern, L. P. Witnauer, C. R. Eddy and W. E. Parker, *THIS JOURNAL*, **77**, 5537 (1955).

The following reference diagram is shown for the analysis of the moment values



The bond moment values may be symbolized as $\text{H}-\text{C} = a$, $\text{C}=\text{O} = b$, $\text{C}-\text{O} = c$, $\text{H}-\text{O} = d$, and the bond angles, $\text{C}-\text{O}-\text{O} = \theta_1$, $\text{H}-\text{O}-\text{O} = \theta_2$, $\text{C}-\text{C}-\text{O} = 90^\circ + \alpha$, $\text{O}=\text{C}-\text{O} = 90^\circ + \beta$. In view of the planarity of $\text{C}-\text{C}-\text{O}$ groupings, only two dihedral angles are needed. The first, ω , is taken in a clockwise direction looking along the $\text{C}-\text{O}$ axis from C to O for measurement of rotation of the acyl group out of the plane containing the $\text{O}-\text{O}$ axis. The other dihedral angle, ϕ , is measured in a clockwise direction looking along the $\text{O}-\text{O}$ axis from right to left for rotation of the $\text{O}-\text{O}-\text{H}$ plane out of the $\text{C}-\text{O}-\text{O}$ plane. The reference diagram shows ω and ϕ both

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$$\mu^2 = [(b \cos \beta + a \cos \alpha) \cos \omega - d \cos (180 - \theta_2) \cos (\theta_1 - 90) - d \sin (180 - \theta_2) \sin (\theta_1 - 90) \cos \phi]^2 + [d \sin (180 - \theta_2) \sin \phi + (b \cos \beta + a \cos \alpha) \sin \omega]^2 + [d \cos (180 - \theta_2) \sin (\theta_1 - 90) - d \sin (180 - \theta_2) \cos (\theta_1 - 90) \cos \phi - (c - b \sin \beta + a \sin \alpha)]^2$$

To study the puckering, *i.e.*, the effect of ω and ϕ on the moment, the bond angles and bond moments can be taken the same as in diacyl peroxides,⁹ dialkyl peroxides and alkyl hydroperoxides,^{9,10} namely, $a = 0.4$, $b = 2.3$, $c = 0.62$, $d = 1.71$, $\alpha = 20^\circ$, $\beta = 35^\circ$ and $\theta_1 = \theta_2 = 105^\circ$. The formula then becomes

$$\mu^2 = [2.2599 \cos \omega - 0.4275 (1 + \cos \phi)]^2 + (1.6517 \sin \phi + 2.2599 \sin \omega)^2 + (0.67695 - 1.5954 \cos \phi)^2$$

According to this formula, free rotation simultaneous about both axes gives the molecular mo-

ment value 2.91 D, showing that the $p\pi$ -electron repulsive forces of the two peroxy oxygen atoms combined with the hydrogen bonding prevent such rotation. If rotation of the acyl group is tried with ϕ fixed, the values 2.51 D for $\phi = 0^\circ$ and 2.96 D for $\phi = 100^\circ$ result. This indication that rotation of the acyl group is restricted would be anticipated from the effects of the hydrogen bonding, the double bond character of the $\text{C}-\text{O}$ link, and, for the case of $\phi = 0^\circ$, on steric grounds.

With ω fixed at 0° , the moment is 3.23 D for free rotation about the $\text{O}-\text{O}$ axis, showing not only that this type of rotation is excluded but also that the dihedral angle ϕ must be less than 90° .

Giguère and Olmos⁴ made their calculations for the model for which $\omega = 0^\circ$ and $\phi = 0^\circ$, but with $\theta_2 = 100^\circ$ instead of 105° . For this planar model we calculate the moment 1.83 D, which is nearly 0.5 D less than the observed value. No reasonable changes in the bond moments for the $\text{O}-\text{H}$ and $\text{C}=\text{O}$ links or in the bond angles will bring the moment of this model close to 2.32 D. The observed value would require that, taken separately,

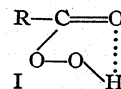
TABLE I

THE DIELECTRIC POLARIZATION, MOLAR REFRACTION AND DIPOLE MOMENT OF ALIPHATIC PERACIDS IN BENZENE

Peracid	Temp., °C.	ϵ_{10}	α	V_{10}	β	n_{D10}^2	γ	P_{20}	M_{RD}		
									Obsd.	Theor.	μ
Perpelargonic (C_9)	30	2.2629	3.175	1.1528	-0.0759	160.9	...	47.49	2.38
	30	2.2629	3.146	1.1529	-.0745	160.0	...	47.49	2.37
Percapric (C_{10})	30	2.2630	2.664	1.1526	-.0742	155.6	51.93		2.27
	30	1.1519	-.0665	2.2330	-0.196	...	51.93	52.11	..
Perlauric (C_{12})	30	2.2624	2.285	1.1527	-.0467	2.2355	-.223	165.0	60.5	61.34	2.28
	30	1.1519	-.0402	2.2329	-.239	...	59.5		..
	50	2.2231	2.227	1.1817	-.0614	165.9	60.5		2.36
Permyristic (C_{14})	30	2.2626	1.978	1.1526	-.0357	172.8	68.8	70.59	2.27
	30	1.1522	-.0378	2.2334	-.224	...	68.8		
Perpalmitic (C_{16})	30	2.2630	1.888	1.1531	-.0748	2.2325	-.152	184.9	78.2	79.81	2.30

the $\text{H}-\text{O}$ moment must go up to 2.9 D or the $\text{C}=\text{O}$ moment to 3.2 D or θ_2 must be reduced to 65° . We may conclude that this model in which hydrogen bonding has completely overcome the $p\pi$ -electron repulsion is not correct.

Apparently, with $\omega = 0^\circ$, ϕ lies somewhere between 0 and 90° and, using the formula above, we find that the spread of ϕ values accounting for the range of observed moments is rather narrow. The mean value corresponding to the mean moment 2.32 ± 0.04 D is $72 \pm 4^\circ$. This configuration with $\omega = 0^\circ$, $\phi = 72^\circ$, will be pictured as model I

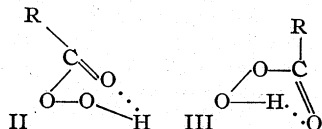


Model I appears to be a reasonable one in terms of the various factors known to be active in determin-

ing the structure of peracids. In it, the $\text{C}=\text{O}$ links are coplanar as expected from the double

(10) M. T. Rogers and T. W. Campbell, *THIS JOURNAL*, **74**, 4742 (1952).

bond character of the bond joining the carbonyl carbon atom to the peroxy oxygen atom, as confirmed by the earlier results for diacyl peroxides.⁹ The 72° bending of the O-H link out of this plane represents a reasonable result of the effect of the hydrogen bonding on the barriers to rotation ordinarily present in peroxides. This relocation of the position of minimum potential energy should



be accompanied by a lowering of the *cis* barrier and a heightening of the *trans* barrier. Using the bond lengths and bond angles proposed by Giguère and Olmos, but with $\theta_2 = 105^\circ$, the O.....H distance is 2.53 Å. in model I.

Using the formula, only two other models, II

and III, were found to have molecular moments equal to the observed value.

In II, both the acyl group and the O-H link are twisted out of the C-O-O plane, and¹¹ if $\phi = 100^\circ$, then $\omega = 345^\circ$. In III, the acyl group alone is twisted out of plane, ω being 70° , $\phi = 0^\circ$.

It is possible that the opposition between the hydrogen bond and the $p\pi$ -electron repulsion might cause the small amount of twisting pictured for the acyl group in model II, but it is hardly likely that at the same time ϕ would be unaffected. On the other hand, model III can have no reasonable basis. We may conclude from the measurements reported here that the actual structure is a puckered one, rather close to model I, with ϕ less than 100° and ω very nearly 0° .

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(11) Each of these three puckered models has an equivalent non-superimposable mirror image, the one in this case has $\phi = 260^\circ$, $\omega = 15^\circ$.